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DEVELOPMENT OF SINGLE CRYSTAL CERAMIC FIBERS

by

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16. Abstract

Exploratory fiber growth and characterization studies were carried out with MgO, doped TiC and heavily Cr_2O_3 doped Al_2O_3 fibers during this program. Single crystal fibers were grown using a CO_2 laser heated, floating zone fiber growth process which was developed principally under the sponsorship of NASA-Lewis.

A unique high pressure growth chamber permitted MgO fibers to be grown from stoichiometric melts for the first time. Vaporization rates were suppressed with high oxygen partial pressures.

Titanium carbide and Cr_2O_3 doped Al_2O_3 fibers were grown from hot pressed or sintered polycrystalline feed rods. The qualities of these fibers were below expectation due to materials processing or handling procedures. In the case of the carbides, a coating on the fibers resulted in relatively low strengths. It could have been eliminated with after heaters. In the case of the Cr_2O_3 doped Al_2O_3, high Si and Ti impurity levels resulted in poor fiber quality due to loss of solidification interface stability. These impurities can be eliminated with modified handling procedures.

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I. SUMMARY

Exploratory fiber growth and characterization studies were carried out with MgO, doped TiC and heavily Cr_2O_3 doped Al_2O_3 fibers during this program. Single crystal fibers were grown using a CO_2 laser heated, floating zone fiber growth process which was developed principally under the sponsorship of NASA-Lewis.

A unique high pressure growth chamber permitted MgO fibers to be grown from stoichiometric melts for the first time. Vaporization rates were suppressed with high oxygen partial pressures.

Titanium carbide and Cr_2O_3 doped Al_2O_3 fibers were grown from hot pressed or sintered polycrystalline feed rods. The qualities of these fibers were below expectation due to materials processing or handling procedures. In the case of the carbides, a coating on the fibers resulted in relatively low strengths. It could have been eliminated with after heaters. In the case of the Cr_2O_3 doped Al_2O_3, high Si and Ti impurity levels resulted in poor fiber quality due to loss of solidification interface stability. These impurities can be eliminated with modified handling procedures.

Three program tasks were undertaken concurrently during this program. The program was terminated without prior notice for the convenience of the Government. As a result, none of the individual tasks were completed as planned.

II. INTRODUCTION

During three contracts with NASA-Lewis, a floating zone fiber growth process has been developed for producing fibers of previously unprocessable or unique quality materials. The fibers are intended for reinforcement of metal matrix composites under development for turbine blade applications.

During the second contract, a CO_2 laser heat source was developed because it imposed no atmosphere restrictions and possessed many intrinsic advantages. When combined with the advantages of a floating zone fiber growth process, the laser heat source gives a unique experimental process for surveying candidate fiber materials. This program was intended to continue growth and characterization of previously unavailable materials as well as the improvement of materials which had previously exhibited outstanding high temperature properties. The program was terminated without prior notice for the convenience of the Government.* The abrupt termination of our experimental work on three of the four tasks left all tasks incomplete. Thus, this report is presented as a statement of our accomplishments and the status of work in progress as of the termination date. It is not intended to represent the reporting of a completed piece of work. All of the objectives were met in the other two programs, and there is every reason to believe they would have been met on this program if it had been completed.

The program consisted of four tasks. Their objectives and approximate portion of the program were:

TASK I (15%)	Grow and characterize undoped MgO single crystal fibers.
TASK II (35%)	Contingent on successful completion of Task I, grow doped MgO fibers to improve high temperature properties. If Task I was not successful, this portion of the program was to be utilized for exploratory work such as growth of fibers with eutectic compositions, etc.
TASK III (17.5%)	Grow and characterize doped TiC fibers.
TASK IV (32.5%)	Grow and characterize heavily Cr_2O_3 doped Al_2O_3 fibers.

During the program, work proceeded on Tasks I, III and IV simultaneously. In this report, each task will be discussed separately.

*Due to funding limitations

III. FIBER GROWTH AND EVALUATION PROGRAM

A. Apparatus - General

The CO_2 laser heated fiber growth apparatus and analytical descriptions of the process have been described in detail[1,2] previously and will only be reviewed briefly here.

Fibers are grown from a CO_2 laser heated floating zone melt which is supported between the feed rod and fiber by the surface tension of the liquid. High purities are possible, since the melt does not come into contact with foreign materials. The CO_2 laser heat source permits virtually complete freedom in selection of ambient atmospheres. This is used to advantage in the program for controlling valance state of dopants and impurities as well as the elimination of impurities.

The CO_2 laser beam is expanded to two diameters by a lens and mirror combination and divided into two beams with a dielectric coated GaAs beam splitter which are brought into the optical bench shown in Figure 1. This optical bench physically divides each of the two circular beams into two semicircular beams. The four semicircular beams are deflected to 5-inch focal length spherical mirrors which focus the beams onto the region of the floating zone melt. Energy density can be adjusted by varying the zone to mirror distance.

The optical bench is shown in position in the controlled atmosphere furnace chamber in Figure 2. Also shown in this figure is the spherical radiation shield used to refocus all of the emitted and reflected radiation back onto the region of the molten zone. This shield proved extremely valuable with the highly reflective, high melting point carbides.

Feed rods are inserted and fibers withdrawn by means of ADL Crystal Pulling heads. The maximum fiber length is approximately 20 cm (8 inches) with the existing fiber withdrawal mechanism.

The diameter of the fiber is controlled by adjusting the relative insertion and withdrawal rates. Fiber diameter variations are caused primarily by variations of the mass flow rate of the feed into the molten zone due to density and dimension variations of the feed rod. We have found that fiber diameters are more uniform than the feed because an averaging process occurs. The axial diameter variation of a nominally 0.1 cm (0.040 inch) sapphire fiber will typically be of the order of 2.5μm (0.0001 inch). The single crystal fibers are not usually round; the hexagonal cross section of a c axis sapphire results from the development of prismatic growth facets. This tendency of single crystal fibers to facet appears general; however, it becomes less apparent as fiber diameters are reduced.

The crystallographic orientation of the fibers is readily defined. Seeding is done in a conventional manner by initiating growth from an oriented single crystal. The orientation may be established by sectioning an

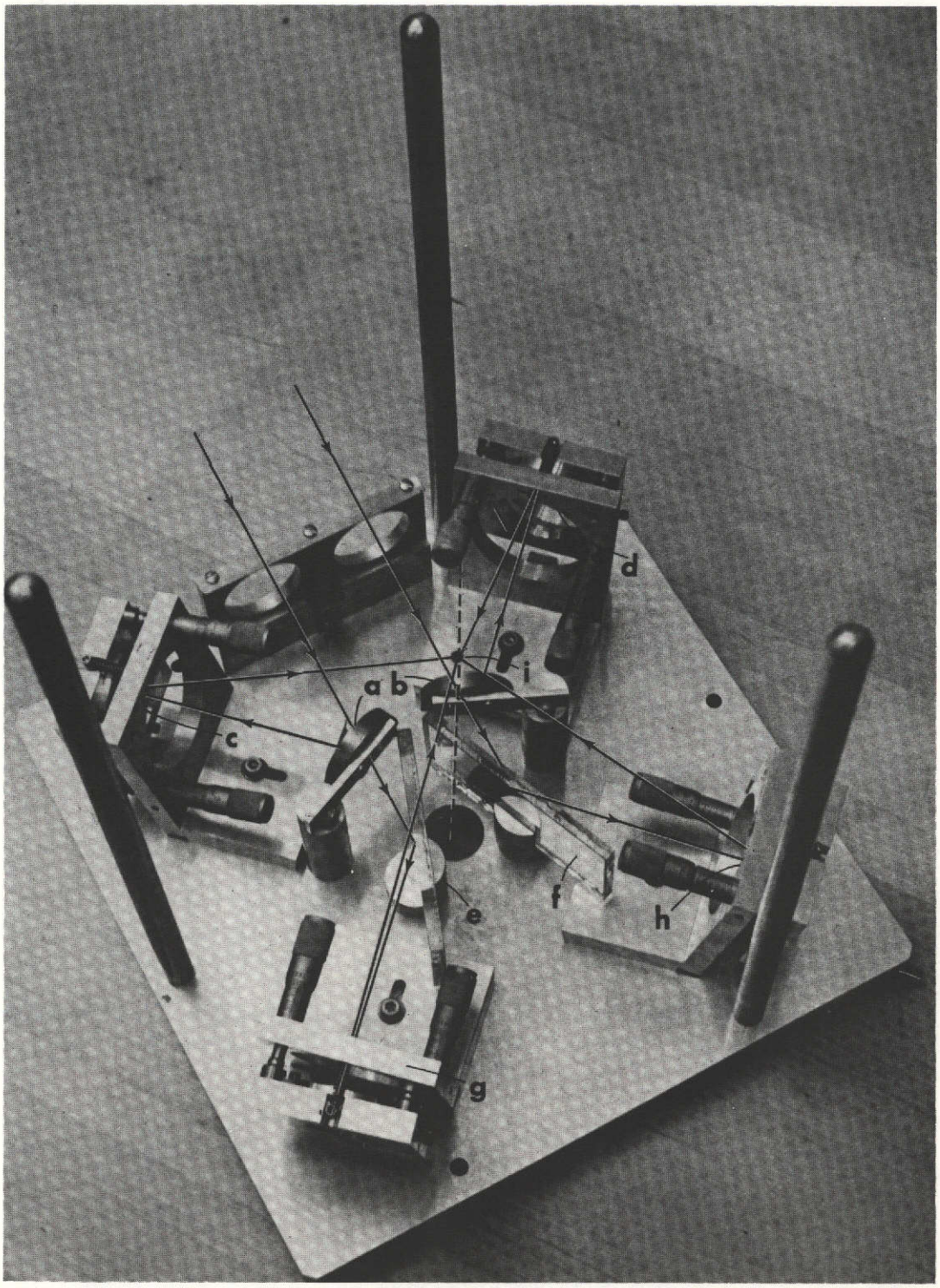


Figure 1 Optical Bench Used in CO_2 Laser-Heated Fiber Growth Process. Input Rays are Divided by Mirrors a and b and Ultimately Focused on i by Mirrors c, d, g and h.

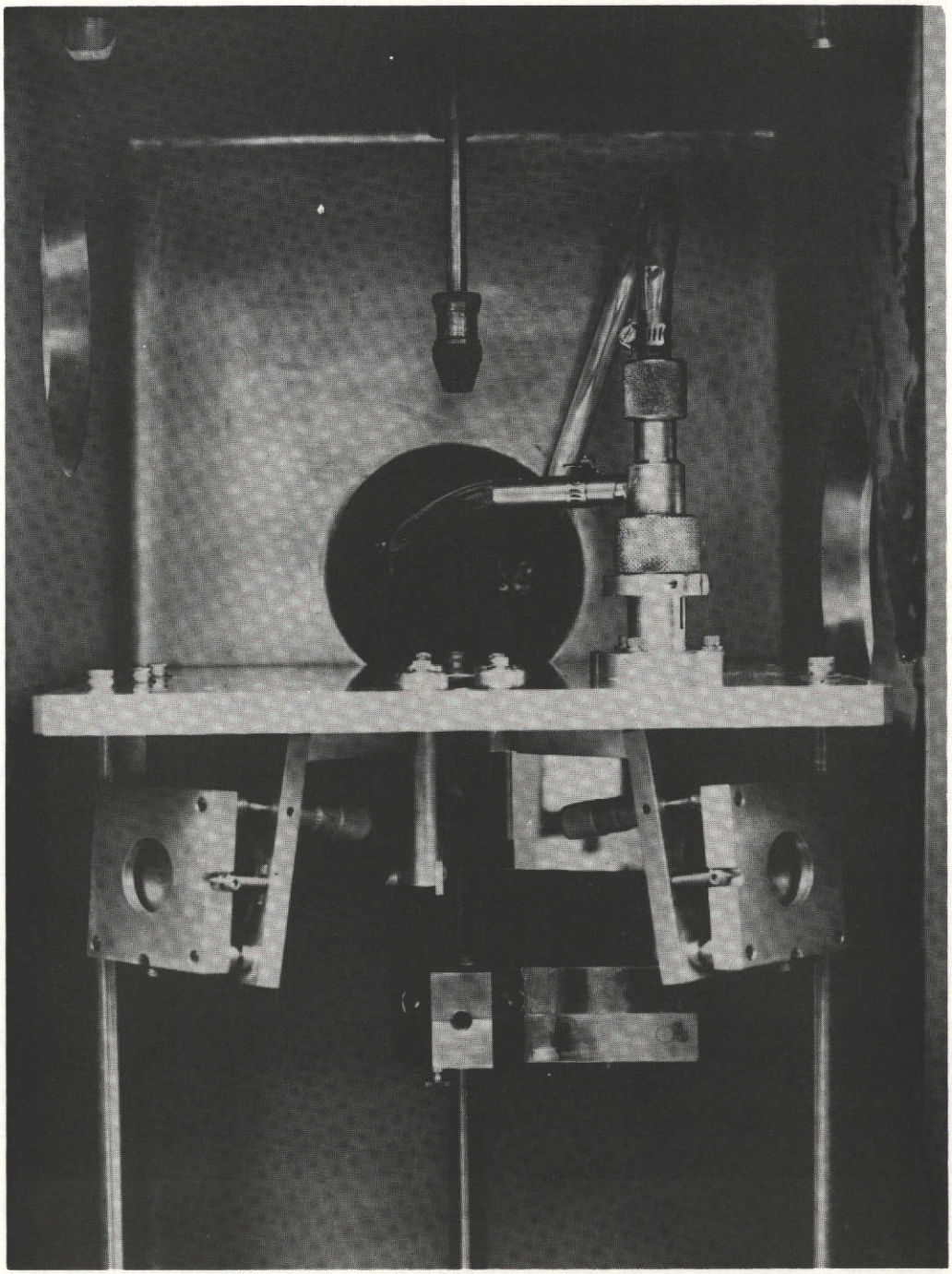


Figure 2 Optical Bench Shown in Position in Fiber Growth Furnace. Water Cooled Spherical Radiation Shield is Shown in the Operating POsition Below the Optical Bench.

oriented seed from a crystal or initiating growth from a single crystal fiber mounted in a goniometer. The latter technique is generally used, since it is so much easier. Growth has been initiated from fibrous seeds oriented 90° to the growth axis.

With small diameter fibers, the surface tension forces exceed gravity forces to an extent that the zone shape is not effected by the direction of pull. Up, down or horizontal growth processes have the same zone shape. Down-pull processes generally produce better quality fibers, since gas bubbles in the molten zone tend to migrate away from the solidification interface. Also, there is less condensation on surfaces of the fibers.

B. Specific Materials

1. MgO (Task I)

Hot pressed MgO feed materials were purchased from Cerac Co., and obtained from the AVCO Co. The Cerac material is reported to be 99.95% pure and the AVCO material 99.9995%. The principal impurities reported in the Cerac material were Si, Ti and Mn at levels from 0.001 to 0.01 weight percent. The AVCO sample was not accompanied by a chemical analysis; however, the feed powder originated from Johnson Mathey. The Cerac sample was pressed to 94% of theoretical density and the AVCO sample to 99.5% of theoretical. These hot pressed disks were cut into 0.16 cm (1/16 inch) square cross section feed rods.

Initial attempts to grow MgO fibers can only be described as marginally successful at best. Excessively high vaporization rates made the process virtually uncontrollable. Vaporization losses can generally be reduced to acceptable levels by three techniques--lowering the growth temperature via a flux growth process, physically suppressing vaporization with high inert-gas pressures and reducing the driving force for vaporization by using high active-gas pressures. Flux growth processes were not pursued for several reasons including low growth rates, poor microstructural quality and a reduced melting point compared to the material grown from the congruent melting composition. Using high gas pressures was believed to be a reasonable course of action.

A literature review revealed a previously unknown estimation[3] of MgO vaporization rates as a function of the oxygen partial pressure in the ambient gas. Magnesium oxide is believed to vaporize according to

$$MgO(\ell) \rightarrow Mg(v) + 1/2\ O_2(v);$$

thus, increased oxygen pressure tends to suppress the MgO loss rate. The calculated effect of oxygen pressure on the MgO vaporization rate is summarized in Figure 3. In addition to the rate reduction which results from a decreased driving force for vaporization, a further reduction can be anticipated with elevated pressures due to impediment of the diffusing species through the boundary layer. This effect was shown[4] to be: vaporization rate proportional to $P^{-1/2}$, where P is the pressure of the ambient gas.

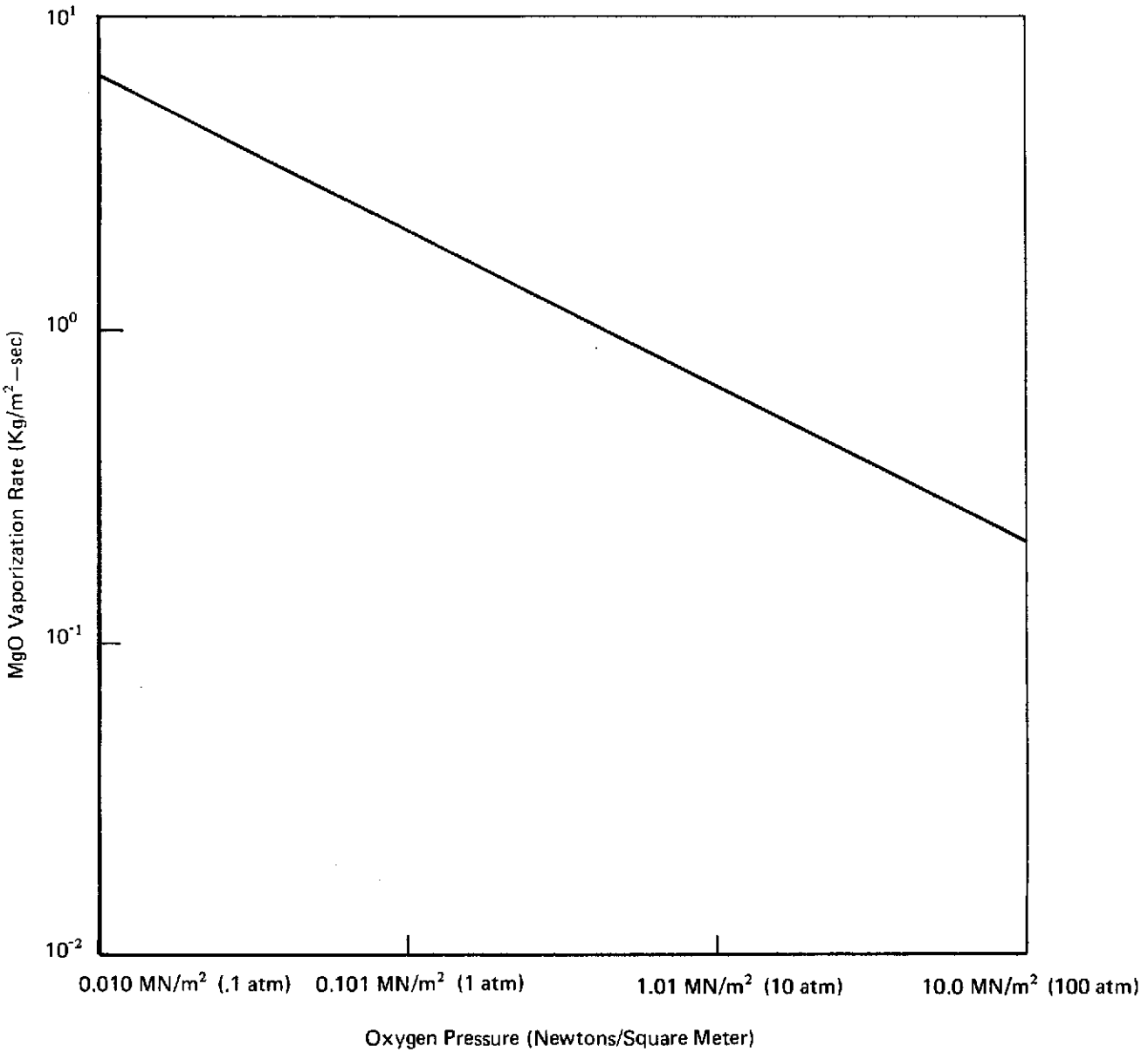


FIGURE 3 **CALCULATED MgO VAPORIZATION RATE AS A FUNCTION OF OXYGEN PRESSURE AT THE MELTING POINT OF MgO 3123°K (2850°C)**

The high pressure fiber growth chamber shown in Figure 4 was constructed to attempt controlling the MgO fiber growth process. It was designed for 10-13 MN/m^2 (100 atmospheres) operation and has been hydrostatically proof-tested at 20-26 MN/m^2 (200 atmospheres). The small chamber occupies the same position in the optical bench and watercooling system used with the spherical radiation shield developed under NAS3-14328. The CO_2 radiation enters the cell and the process is viewed through O-ring sealed KCl windows. The basic features of the chamber are obvious from the photograph. The shafts are sealed to the tubes by O-rings similar in detail to those used in the ADL-Crystal Pulling Heads.

One ruby fiber was grown in the high pressure chamber to provide a basis for comparison with previous fiber quality. There was no apparent reduction in quality. In fact, the shaft seals improved shaft alignment and reduced vibration.

One MgO growth run was made in the high pressure chamber using Cerac feed stock. The chamber was pressurized to 0.69 MN/m^2 (100 psig) with O_2 and then to 3.45 MN/m^2 (500 psig) with N_2. The process was controllable with the combined effects of an elevated O_2 partial pressure 0.67 MN/m^2 (6.65 atmospheres) and a high inert ambient gas pressure. Growth rates were varied from 2.54 to 25.4 cm (1 to 10 inches) per hour and attenuation ratios from 1/1 to 10/1. Vaporization losses were still high; however, the process was controllable. It is expected that good quality MgO fibers can be produced by this technique.

Higher pressures were not utilized because the growth chamber had not been equipped with a rupture disk and also it overheated. The use of a rupture disk was felt necessary to avoid an explosion if organic material was inadvertently introduced into the high pressure O_2 environment. Overheating was eliminated by using a Cu sleeve in the chamber, using a Cu flange on the upper tubulation and adding watercooling to the upper tubulation.

The 13.79 MN/m^2 (2000 psi) rupture disk assembly was installed, but growth runs with higher oxygen pressures were not undertaken because the contract was terminated.

The limited experiments with MgO indicate that fiber growth from stoichiometric melts is possible with high oxygen pressures.

Property measurements were not initiated with the small sections of MgO fibers which were grown because it was believed longer, higher quality pieces would be grown later in the program. Microstructural and surface observations revealed that the fiber sections were pore-free, single crystal and smooth. They had the essential properties required for good mechanical properties.

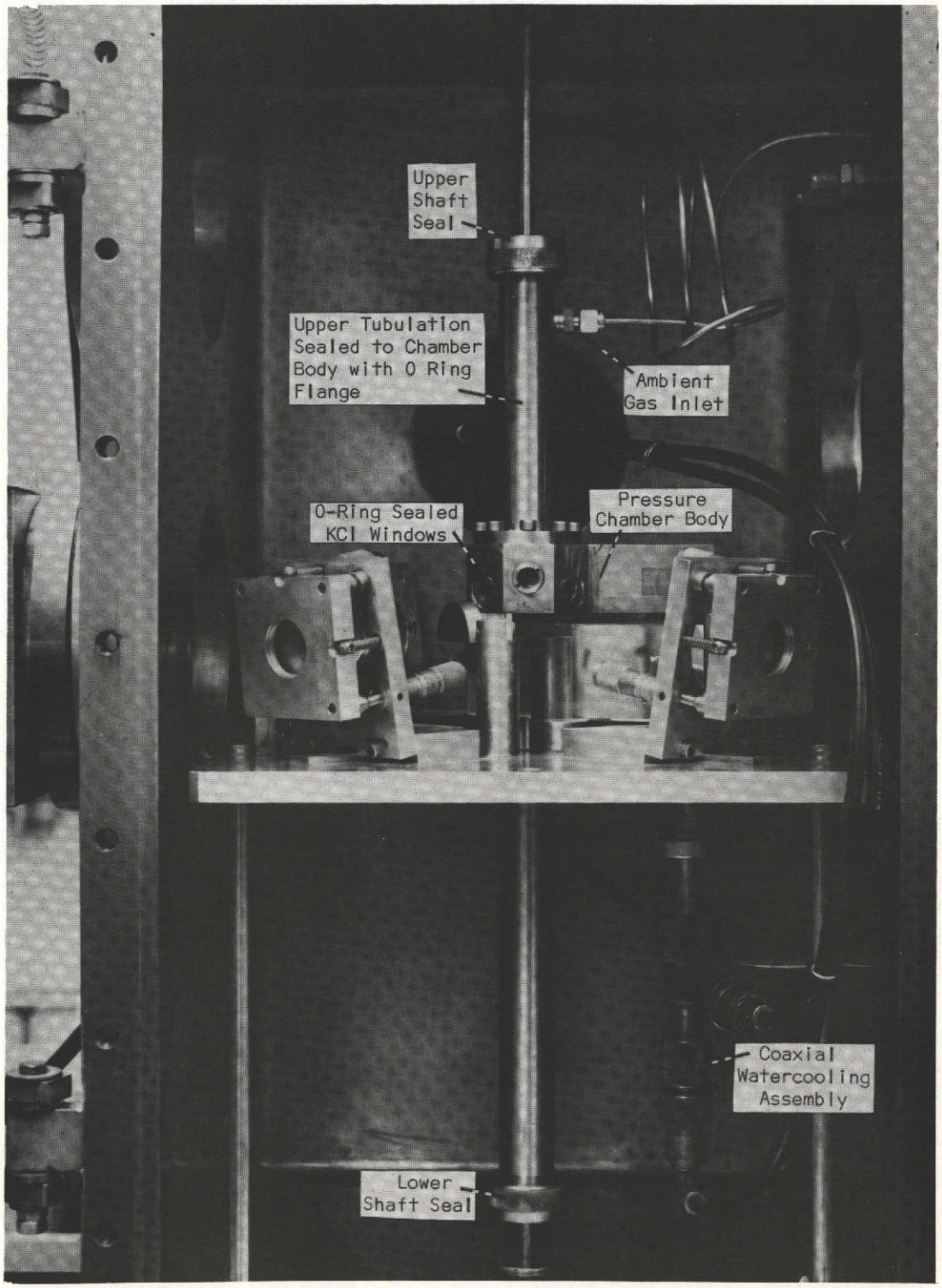


FIGURE 4 High Pressure Fiber Growth Chamber Positioned in Optical Bench Developed for CO_2 Laser Heated Fiber Growth Apparatus

2. Doped TiC (Task III)

Undoped TiC single crystal fibers were grown successfully previously[2] although deficiencies in the feed material made control of the process marginal. Room temperature and elevated temperature strengths were high enough to project adequate composite properties if rule of mixture properties could be achieved. It was obvious that the quality of the feed stock should be improved to give better process control and that strengths should be raised to allow for deterioration during fabrication. Based on reported mechanical properties and solidification criteria, a boron doped TiC_{1-x} composition and two TiC/VC Alloys were selected and ordered from Cerac Inc.

The effect of boron on the yield strength of TiC has been studied extensively[5,6] in the past. Boron concentrates at extrinsic dislocation nodes where small [approximately 10Å] TiB_2 precipitates form, pinning the dislocations. A ten-fold increase in yield strength was observed with less than 1000 ppm of B. This carbide exists over a range of carbon deficient stoichiometries from 32 to 49.4 atomic percent carbide (Figure 5[7]). With undoped, high purity single crystals, the yield strength decreases continuously with decreasing carbon content. Thus, there is an obvious temptation to grow nearly stoichiometric fibers. We selected the congruent melting point composition (44 atomic percent carbon) since high solidification rates can be maintained at this composition without the mass transport required in noncongruent solidification processes. Three hot pressed disks with Ti/C ratios corresponding to $TiC_{.785}$ were ordered. One was undoped, the other two were doped with B at 1 and 5 weight percent. We anticipated that much of the boron would be lost by vaporization so that the retained levels will be close to those previously achieved by diffusion processes.

Two TiC-VC alloys selected were on the VC-rich side of the pseudo-binary phase diagram. The 75% VC, 25% TiC composition was selected to duplicate the results shown in Figure 6.[6] This composition does not melt congruent; thus, it may present some problems in growing fibers at high rates. The second TiC-VC alloy selected ($Ti_{.16}V_{1.126}V$) is the congruent melting composition for the mixed carbides in the Ti-V-C ternary system (Figures 7 and 8[8]). From solidification criteria, this is the best composition. Some compromise will ultimately be required between mechanical properties and processing requirements.

Characterization of the carbide feed stock purchased from Cerac included emission spectrographic analyses and X-ray diffraction analyses for phase identification and determination of the TiC lattice parameter. The latter was determined to permit estimation of the Ti/C ratio in the TiC phase of the feed stock.

A summary of the feed rod characterization completed to date is given in Table I. The emission analyses indicate that the feed rods are probably acceptable from the standpoint of elements this technique reveals. We

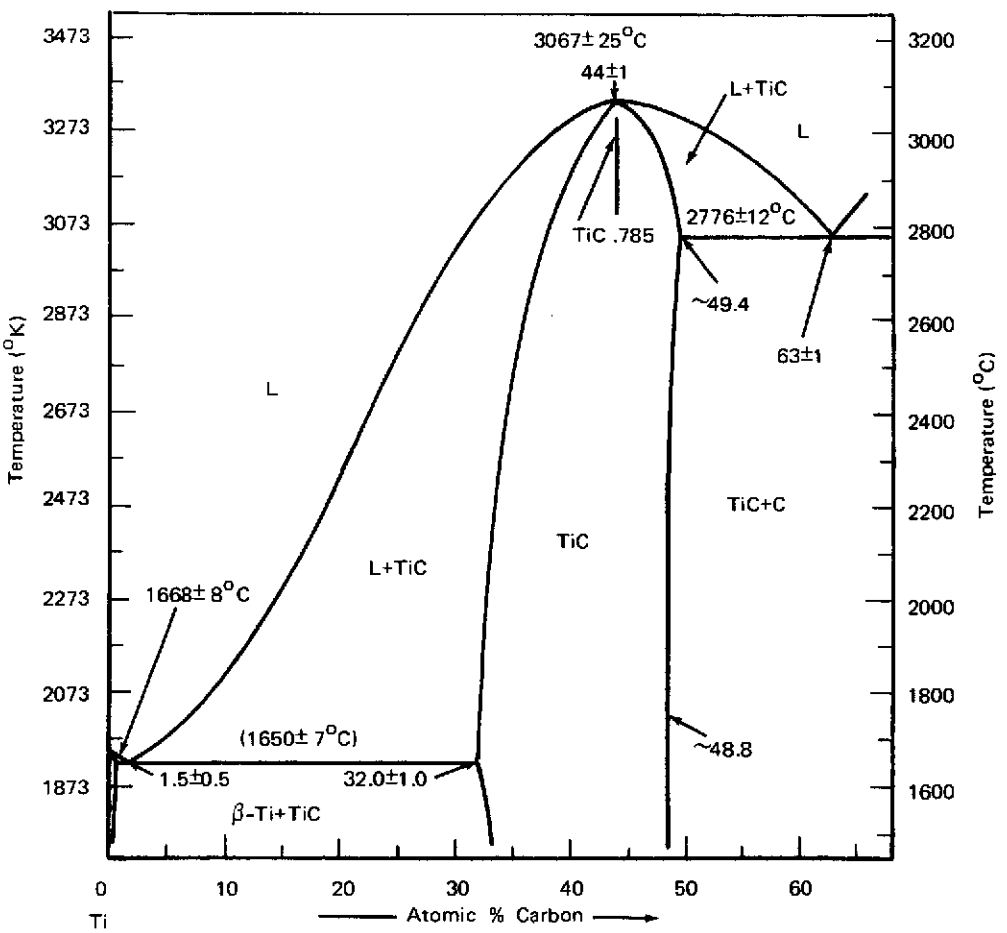


FIGURE 5 CONSTITUTION DIAGRAM OF THE SYSTEM Ti–C
(Temperature Error Figures Based On Estimated Overall Uncertainty)

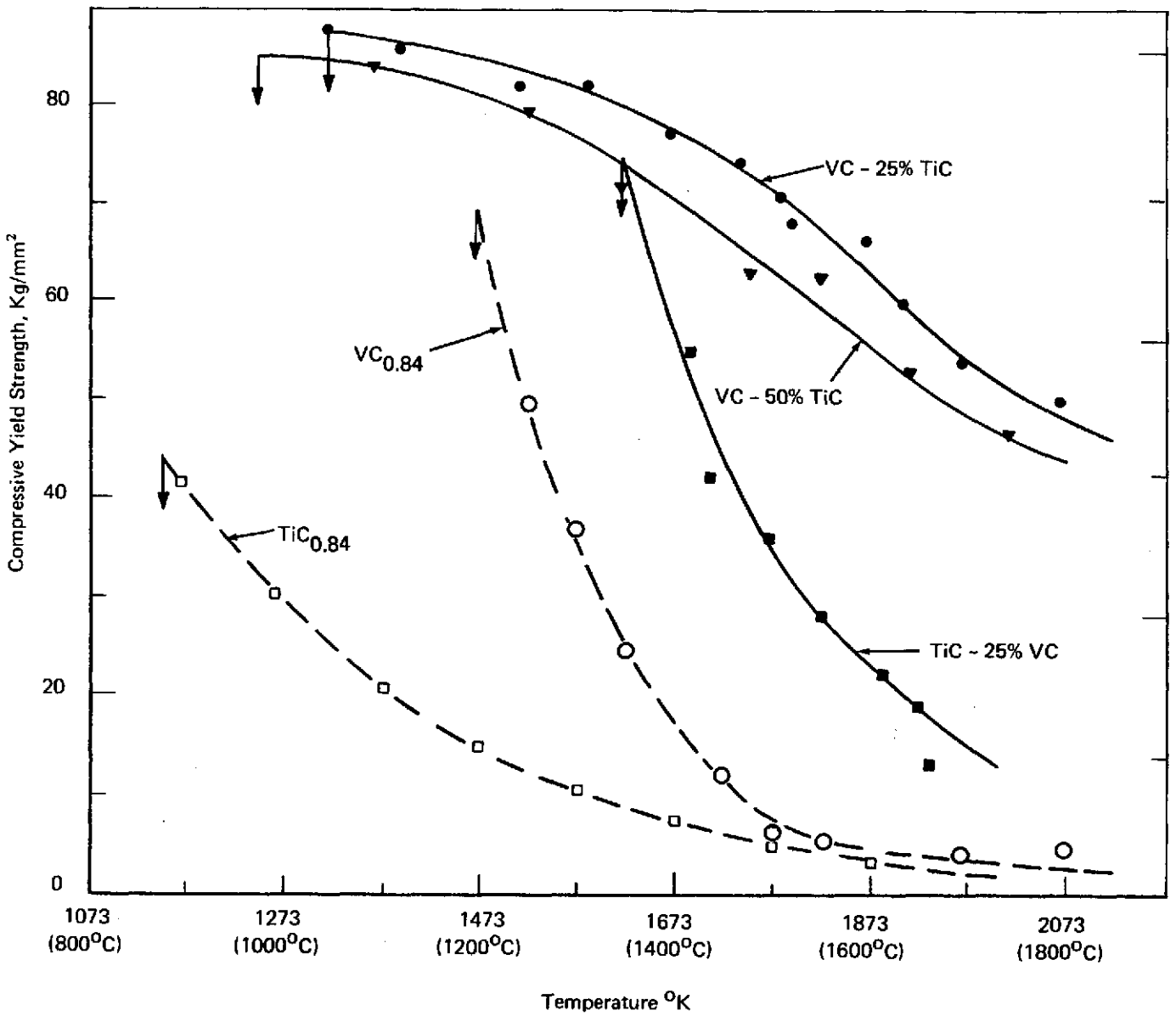


FIGURE 6 THE YIELD STRENGTH (<001> COMPRESSION) AS A FUNCTION OF TEMPERATURE FOR SOME TiC–VC ALLOYS, COMPARED WITH THAT OF $TiC_{0.84}$ AND $VC_{0.84}$

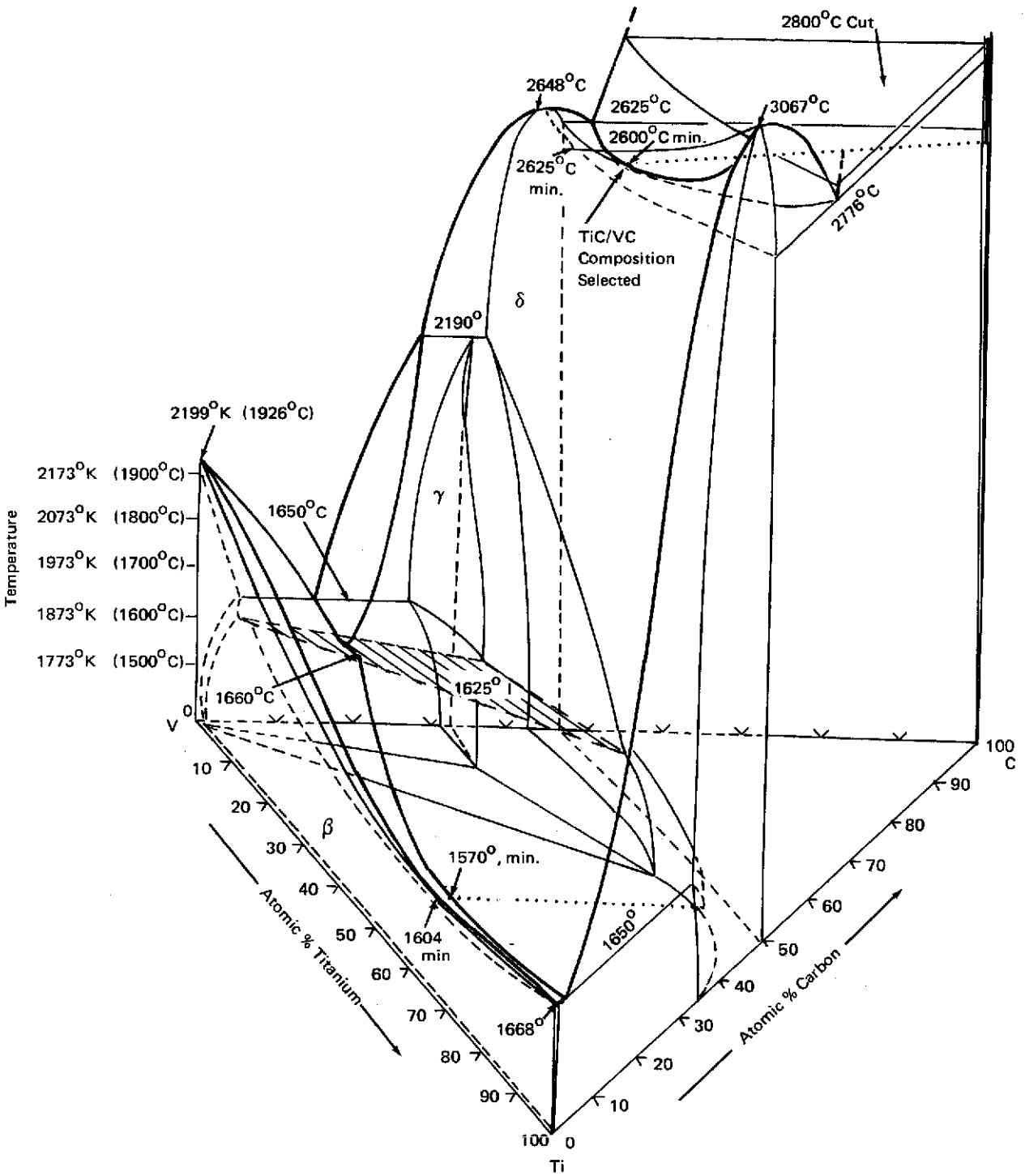


FIGURE 7 ISOMETRIC VIEW OF THE Ti-V-C SYSTEM

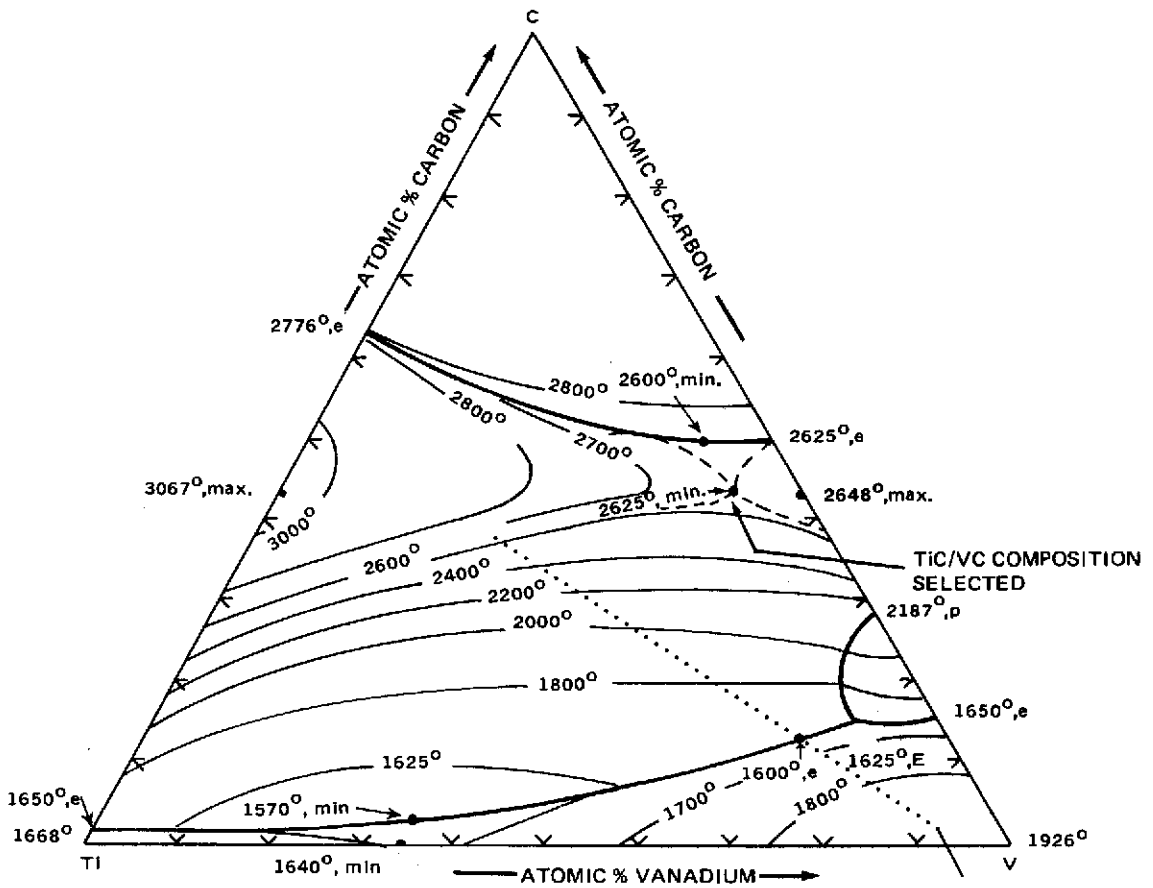


FIGURE 8 LIQUIDUS PROJECTS IN THE Ti–V–C SYSTEM
DOTTED: PSEUDOBINARY EUTECTIC LINE

TABLE I

SUMMARY OF CERAC FEED ROD CHARACTERISTICS

DISK	HP-4963	HP-4965	HP-4966	HP-4967	HP-4964
Mixture	94.9w/o TiC 5.1w/o Ti	94.9w/o TiC 5.1w/o Ti + 1w/o B	94.9w/o TiC 5.1w/o Ti + 5w/o B	75w/o VC 25w/o TiC	81.3w/o VC 10w/o Ti 8.7w/o V
X-ray Phases	TiC	TiC, TiB_2	TiC, TiB_2	--	--
TiC Lattice Parameter(Å)	4.3285	4.3252	4.3262	--	--
Emission Spectrographic Analysis					
>10%	Ti	Ti	Ti	V	V
3-30%	--	--	--	Ti	Ti
.3-3%	--	B	B	--	--
100-1000ppm	Co,W*	Co,W*	Co,W*	Co	Co
30-300ppm	Cr	Cr	Cr	Cr	Cr
10-100ppm	Fe	Fe	Fe	Fe	--
3-30ppm	--	--	Si	Ca,Cu,Si	Fe
1-10ppm	Mo,Ni,Si,Zr	Cu,Ni,Si,Zr	Ca,Cu,Ni,Zr	Mg,Ni	Cu,Ni
.3-3ppm	Cu,Sn	Ca,Mg,Mo,Sn	Mg,Mn,Mo,Sn	Al,B,Mn,Mo	Mo,Si
.1-1ppm	Ca,Mg,Mn	Mn	--	--	Mg,Mn
Theoretical Density	4.779	4.728	4.545	5.444	5.572
Measured Density	3.788	3.578	3.246	4.532	4.061
Porosity	21%	25%	29%	17%	28%

*Tungsten levels uncertain.

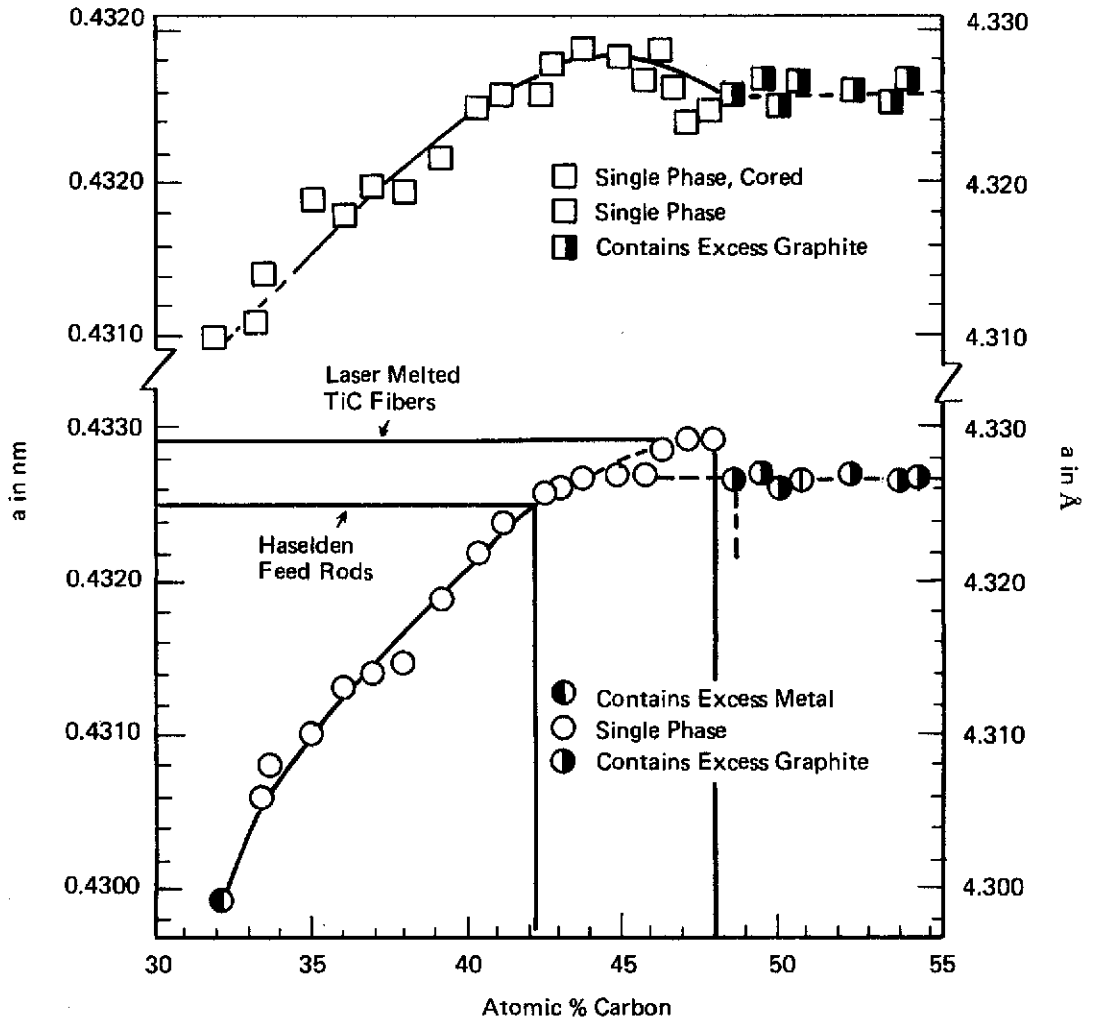
have previously grown single crystals from feed rods of this approximate purity level without difficulty. Most impurity levels decrease 1 to 3 orders of magnitude by vaporization from these extremely high temperature melts. High porosities are a significant deficiency of these feed rods.

The lattice parameters of the TiC phases and the absence of free Ti in the feed rods indicate another problem. These lattice parameters correspond to higher titanium compositions than the congruent melting point.[7] They are larger than were previously observed with the Haselden feed rods.[2] It appears on the basis of these results that all of the free Ti reacted with the graphite dies and/or the metallic B during hot pressing. Furthermore, the Ti/C ratio of the initial TiC powder was not stoichiometric as was indicated by Cerac. The difference between the lattice parameters of HP-4963 and those of HP-4965 and 4966 probably result from the free Ti reacting with the free B rather than the graphite dies; thus, the Ti/C ratio of the remaining TiC is lower in the two latter disks. It is our opinion that the Ti/C ratios in the three TiC base disks are higher than were ordered and are higher than the Haselden rods used previously.[2] It also appears that the stoichiometry-lattice parameter relationship in the hot pressed rods is more accurately described by the upper curve in Figure 9[9] than the lower curve as was assumed previously.

The lattice parameters of TiC fibers grown from the Haselden feed rods were 3.3297Å compared with 4.3303Å observed for single and multiple meltings of the Cerac material. This indicates that the stoichiometries are nearly equal to each other and to that of the congruent melting point composition. The feed rods and fibers of the Haselden material are both somewhat richer in Ti than the Cerac originating materials.

During this program, we were unable to duplicate the fiber quality achieved previously[2] with TiC fibers. In contrast to our previous experience with TiC,[2] the TiC fibers grown from Cerac material all exhibited rough coatings. The coatings were readily visible on the feed rod just above the zone and reforming on the grown fiber 3 to 5 fiber diameters below the zone. The last-to-grow portions of the fiber were always uncoated and had good surface finishes. The cores of the fibers were generally single crystal and were single phase. The weakness of the fibers was attributed to the coatings, since the cores appeared essentially the same quality as TiC fibers originating from Haselden material. The discrepancy between ordered and delivered compositions does not explain the problems we have encountered growing TiC fibers of equivalent quality to those grown previously.

Experiments were initiated to remove the coatings from the fibers after growth and also to prevent, or at least suppress, the coating process during growth. It was recognized that post-growth cleaning was not desirable but it represented an expedient way of determining the potential usefulness of the carbide fibers and, if successful, the cleaning process might help to identify the deposit.



Source: AFML–TR–65–2, Part V, Compendium of Phase Diagram Data, p. 161.

FIGURE 9 LATTICE PARAMETERS OF TITANIUM MONOCARBIDE

Chemical polishes which were investigated included boiling phosphoric acid, one-to-one mixtures of boiling sulfuric-phosphoric acids, boiling Murakamis solution and electrochemically in a 7% perchloric acid-methanol solution at -20°C. At best, the coating was only partially removed, which resulted in non-uniform diameter reduction of the fibers. The coating is electrically conductive, since samples could be examined up to 2000X in a scanning electron microscope without loss of resolution due to charging effects. The post-growth polishing approach was abandoned, since modified growth conditions, which were carried out concurrently, appeared to be making progress.

The growth conditions used initially with the Cerac feed materials differed substantially from these used previously[2] with the Haselden feed rods. Both conditions are summarized in Table II. A Haselden feed rod melted under the initial conditions used with the Cerac material produced a coated fiber. Thus, it was concluded that the modified processing conditions, singularly or in combination, caused the coating. Process conditions were changed, one by one, back to those originally used with little improvement. The exception was inverting the optical bench, which slightly reduced coating thicknesses. In this configuration, the incident beams are depressed from the horizontal, hitting the down-pulled zone at an oblique angle. All of our experience with the oxides indicated that the use of a near normal angle of incidence yielded a more stable process which was the basis of locating the optics on the top of the bench for down-pulling. A TiC fiber was grown from a Haselden feed rod under conditions that duplicated as closely as possible those used in the previous contract.[2] It was coated but not as heavily as those grown from the first melting of the Cerac material. Thus, the actual growth conditions must still have differed in some minor detail.

The only remaining difference between previous and current growth conditions is in procedures used to align the optical bench. Alignment of the zone relative to the center of the spherical cavity and to the incident beams have been substantially improved. With improved alignment, all of the incident CO_2 radiation, the reflected CO_2 beams and the emitted radiation are focused onto a small area. This causes two effects--there is very little afterheating of the fiber or preheating of the feed rod, and the efficiency of the process is extremely sensitive to the position of the molten zone throughout the duration of the growth run. The second factor was definitely observed. Power requirements to maintain a molten zone varied constantly during a run and the zone was lost frequently due to freezing or necking off. The first factor may be the cause of the coating after growth.

It is believed that there was a closed gas circulation path within the sphere because the inside was coated with a deposit which decreased in thickness from the top to bottom. There was no evidence of equivalent deposits on the exterior of the sphere or any other components of the optical bench. Thus, the saturated gas appeared to be swept up along a fiber, grown in a downward direction, where it deposited until a specific

isotherm was reached, where deposition no longer occurred. This isotherm likely corresponds to the point, 3 to 5 fiber diameters below the molten zone where the coating appeared to form. A more diffuse heated zone with less precise alignment would provide afterheating and may have permitted withdrawal of the original fibers from the sphere while they were still too hot to permit condensation of the deposit.

Two runs were made with tungsten afterheaters surrounding the fibers and extended up into the spherical shield. The afterheaters markedly reduced the coating on the fibers; however, we were not able to complete these series of experiments prior to the termination of the contract. These results do substantiate the hypothesis that the coating resulted from a circulating gas within spherical radiation shield.

There was some evidence that the coatings were related to impurities in the feed materials. The coatings were mechanically removed from large diameter fibers which had been grown at slow growth rates. Fibers grown from these mechanically cleaned feed rods had substantially less coating than fibers grown directly from the sintered feed rods or feed rods which had not had the coating removed.

Our understanding of the coating problem progressed,but it was not completely resolved during the contract. The fact remains that smooth, uncoated TiC fibers were grown at one time so they can obviously be grown again once the required processing parameters are defined.

No mechanical testing was performed on these TiC fibers, since the testing program was deferred until the coating problem was resolved. Many of the heavily coated fibers were so fragile that they could not be handled without breaking them. The uncoated and lightly coated fibers appeared to have approximately the same strengths as those grown previously.

3. Doped Al_2O_3 (Task IV)

Chromia (Cr_2O_3) doped alumina (Al_2O_3) feed rods were made up by mixing Adolf Meller (Providence, R.I.) 1μm Al_2O_3 with appropriate quantities of Cr_2O_3. Chromia doping levels were 1, 3, 5 and 10 weight percent. The powders were milled in high alumina ball mills, pressed into rectangular bars (9x15x55mm) and fired at 1873°K (1600°C) for 6 hours. These densified bars were sectioned into 2x2 mm square cross section feed rods. As-fired densities ranged between 50 to 60% of theoretical.

Fiber growth from these square, polycrystalline feed rods was highly controllable. There was some evidence of the feed rod sintering just ahead of the melting interface. Neither the sintering nor the residual porosity in the feed rods presented any problems in growing the fibers.

These fibers were not the same quality as those grown from previously melted or other high purity polycrystalline feed stock. They were more like those grown from commercial polycrystalline feed rods.[1] Internal pores, coring, precipitates and rough surfaces were produced under normal growth rates.

TABLE II

GROWTH CONDITIONS USED IN NAS3-14328
(Haselden) AND NAS3-16784 (Cerac)

VENDOR	HASELDEN	CERAC
Beam Expansion	2X	1X
Fiber to Mirror Distance	15.75 cm (6.2 inches)	11 cm (4.35 inches)
Optics	Above Bench	Below Bench
Alignment Technique	He-Ne Laser and jigs	CO_2 Laser
Atmosphere	Static Ar-5% H_2	Flowing Ar-5% H_2
Feed Stock Density	≈ 100%	≈79%
Feed Rod Shape	Round	Square

Chemical analyses shown in Table III reveal the source of the problem. Silicon and titanium impurities were introduced at very high levels during the mixing process--presumably from the mill and balls. We had previously observed that the low distribution coefficient of Si in Al_2O_3 caused the solidification interface to breakdown,[1,2] which led to coring and rough surfaces. The titanium presented a second problem in growing the ruby fibers because it has a very low distribution coefficient in Al_2O_3 in oxidizing atmospheres which are required with Cr doping. Titania doped sapphire can be grown readily in reducing atmospheres where the titanium is in the @3 valance state and will substitute directly for Al^{+3} but not in the @4 valance state. There is no reason why these fibers should not have been as good as previously achieved if it had not been for the Si and Ti contamination.

The chromium content, by weight, was determined quantitatively for samples given in Table III. The weight percentage Cr_2O_3 is 1.46 times the weight percentage Cr. Thus, the analysis indicated 4.2% Cr_2O_3 in the feed stock rather than the nominal 5% mixture. This difference may or may not be real. Chromia losses during sintering or absorbed water in the Cr_2O_3 feed powders could account for the apparent deficiency if the sample was homogeneous. More significant is the loss of chromia during fiber growth. Approximately 62% of the initial Cr_2O_3 was lost during the first pull and 23% of the remaining Cr_2O_3 was lost during the second pull. The smaller fractional loss can be accounted for by the pull rates. The first pull rate from square cross section feed rods were 2.5 times slower than the "second" pull rate which is approximately the same ratio as the percentage Cr_2O_3 losses in the two cases.

More detailed analyses of these results is not warranted. They do show clearly that high chromia retention in the fibers will require high growth rates. High quality fibers, in turn, can only be grown at high rates if all residual impurities are carefully controlled.

The majority of Cr_2O_3 doped Al_2O_3 fiber growth runs were made with the two higher doping levels (5 and 10 weight percent), since it has been observed that abraded fiber strengths at temperatures in excess of 400°C improve with higher Cr_2O_3 doping levels.[10] The mechanical testing of the Cr_2O_3 doped fibers was limited to room temperature buckling tests.[2] The nominally 5 weight percent fibers exhibited average strengths of approximately 2.756 GN/m^2 (400,000 psi) and the nominally 10 weight percent fibers exhibited average strengths between 2.262 to 2.317 GN/m^2 (328,000 to 336,000 psi). While these strengths are much lower than the best virgin strengths observed for Cr_2O_3 doped Al_2O_3 fibers, they do exceed previously observed abraded strengths by 1.5 to 2 times. We feel that the rough surfaces of these fibers in their "as-grown" condition makes comparison of their strengths with abraded fibers valid. The program was terminated before high temperature strength tests could be made. Based on the results we previously obtained with rough fibers[1] and the results Crane observed[10] with abraded fibers, it is probable that tensile strengths of these fibers at 1366°K (1093°C) would be in the range 50 to 70% of their room temperature strengths. Thus, they may have exhibited better high temprature strengths than have been observed to date.

TABLE III

CHEMICAL ANALYSES OF ALUMINA FEED POWDER, FEED RODS AND GROWN FIBERS DOPED WITH 5 WEIGHT PERCENT Cr_2O_3

Element	Meller Powder	Sintered Feed Stock	Single Pull	Double Pull
Al	Major	Major	Major	Major
Si	3-30	100-1000	30-300	3-30
Fe	3-30	10-100	3-30	1-10
Ca	1-10	3-30	10-100	.1-1
Mg	3-30	30-300	30-300	10-100
Pb	1-10			
Ga	1-10			
Cr	0.1-1	2.85%	1.10%	0.85%
Cu	0.1-1	1-10	.1-1	.1-1
Ti		100-1000	100-1000	30-300
Ba		.3-3	3-30	
Mn		.1-1		

Impurity levels are ppm by weight.

Dopant levels (Cr) are percent by weight.

IV. DISCUSSION OF RESULTS

The discussion of the experimental results will be brief,since no individual task of the program had been completed at the time work was terminated. Optimum processing conditions for each of the materials under consideration simply had not been defined and, in some cases, we had not identified the specific reasons for processing problems.

The laser heated, floating zone fiber growth process did continue to demonstrate its versatility as an exploratory tool for processing materials. For instance, magnesium oxide fibers were grown from stoichiometric melts under conditions that would pose insurmountable experimental problems to other types of processes. This cell will undoubtedly find use with other materials which sublime at low pressures.

The problem with forming coatings on the carbide fibers was not completely resolved, but it does appear probable that post-heating the growing fibers, so that deposition could not occur in or near the spherical radiation shield, would have solved the problem. It is likely that the specific alignment of the optical bench and sphere used in the previous contract[2] did induce post-heating with the laser. We were unable to duplicate an optical alignment which completely achieved the desired result; however, the effect was demonstrated with modified alignments and resistance afterheaters. The results achieved previously can certainly be duplicated once critical processing parameters are adequately defined and controlled. The boron and vanadium doped titanium carbides warrant further investigation.

The results with the heavily chromia-doped Alumina (ruby) fibers were below expectation. The source of the processing problems, high Si and Ti impurity levels, is understood and can be eliminated by appropriate materials handling procedures. There is no reason to believe that the strengths already demonstrated with ruby fibers are optimum, since they basically represent a single chromia content. Besides strength improvements which may be realized with dopant modifications in the sapphire fibers, it is probable that the composition of the fibers can be adjusted to improve their compatability with potential metal matrices. The tailoring of fiber compositions, to improve their chemical compatability with matrices, is one of the most important areas that has to be investigated since fiber strengths are already high enough to project adequate performance if rule of mixture properties are achieved and maintained.

We feel that this program would have met its objectives if it had been permitted to continue for the duration of the contract. It is with genuine regret we reported this work in an unfinished state.

V REFERENCES

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